The Origin and Composition of Pyrolusite Concretions in Hawaiian Soils[1]

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The soils of the drier regions of the Hawaiian Islands have a very high manganese content. Kelley (1909) has reported that certain dark-colored soils which are closely associated with the red soils have an Mn_3O_4 content ranging from 2.4 to 9.7 per cent. He has indicated the relationship between the poor growth of pineapples and the high manganese content of these soils (1909, 1910). In a later publication Kelley (1912) described the occurrence and distribution of the manganiferous soils on the island of Oahu. He pointed out that within the boundaries of the manganiferous soils there were areas of variable sizes where pyrolusite concretions appeared to have accumulated. These areas have been observed by many workers since the publication of Kelley's work. In some of the irrigation ditches it is possible to gather large numbers of these concretions which have been concentrated by the irrigation water.

The origin of these concretions has been the subject of much speculation. Kelley (1912) has suggested two possible hypotheses. The first states that the formation of the concretions took place while the island of Oahu was submerged. This theory is supported by the similarity between the chemical composition of the concretions found in the soils of the island of Oahu and the composition of concretions from the floor of the Pacific Ocean as reported by Murray and Renard (1891). Pyrolusite concretions are often found in the sediments of fresh-water lakes. The second theory of the origin of these concretions is that the manganese has become soluble by the weathering of the basalt lavas and has leached to the lower elevations in drainage waters where it becomes oxidized and is precipitated around various nuclei.

During the summer of 1947 the senior author discovered a large number of pyrolusite concretions formed around the roots of a shrub on the island of Lanai. A closer examination revealed that a thin layer of MnO_2 had been deposited around all of the roots and that concretions had developed at certain points along the root of the plant. The concretions, when separated from the root of the plant, were tubular in shape. Further examination of the concretions in the soil revealed that the majority of them had been formed by their precipitation around roots of plants. As a result of this discovery a study has been made to determine the nature, origin, and composition of pyrolusite concretions occurring in Hawaiian soils.

A number of concretions have been collected from several typical manganiferous soils. In each case evidence was gathered as to the possible origin of the concretion. From these examinations it is very likely that all of the concretions have been formed by the oxidation of soluble manganese and its precipitation around nuclei. The deposition of MnO_2 occurs in root channels, in cracks in the soil, around roots of plants, on surfaces of soil granules, and in the non-capillary pores of the soil. The shape of the concretion is determined by the manner of deposition. The spherical forms have developed where the MnO_2 has been oxidized and depos-

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ited around very small nuclei. The size of the spherical concretions varies from barely visible specks to perfectly rounded balls three-eighths of an inch in diameter. The nature of the growth of these concretions prevents the inclusion of the surrounding soil. In general this type of concretion is scattered uniformly throughout the soil. The concretions which form in root passages, earthworm holes, cracks, and around soil aggregates have irregular shapes. These concretions are rough and have no definite shapes. Some of the concretions formed in this manner do include portions of soil. As mentioned before, the concretions forming around roots have a tubular shape. They are irregular in length and diameter. When the root decays, the opening becomes filled with soil; however, the concretion will continue to grow with the gradual displacement of the soil from the opening. The three types of concretions are shown in Figure 1.

The chemical composition of the manganiferous soil and its concretions was determined by procedures described by Piper (1944). The data obtained from this analysis are given in Table 1. The manganese oxide contents of the three soil samples are very variable; otherwise their chemical composition is quite uniform. The concretions have a very uniform composition. The silica and iron oxide content of the concretions is lower than that of the soil. The alumina content of the concretions would suggest that they contain variable amounts of clay, which in the case of these soils would be of the kaolinite type. The MnO_2 content of the concretions is uniform, varying from 27.9 to 30.8 per cent.

The data given in Table 2 were obtained from the analyses of typical concretions of the spherical, tubular, and irregular types. The chemical composition of the three types of concretions is in general similar. The total oxides are higher in the spherical form, suggesting either

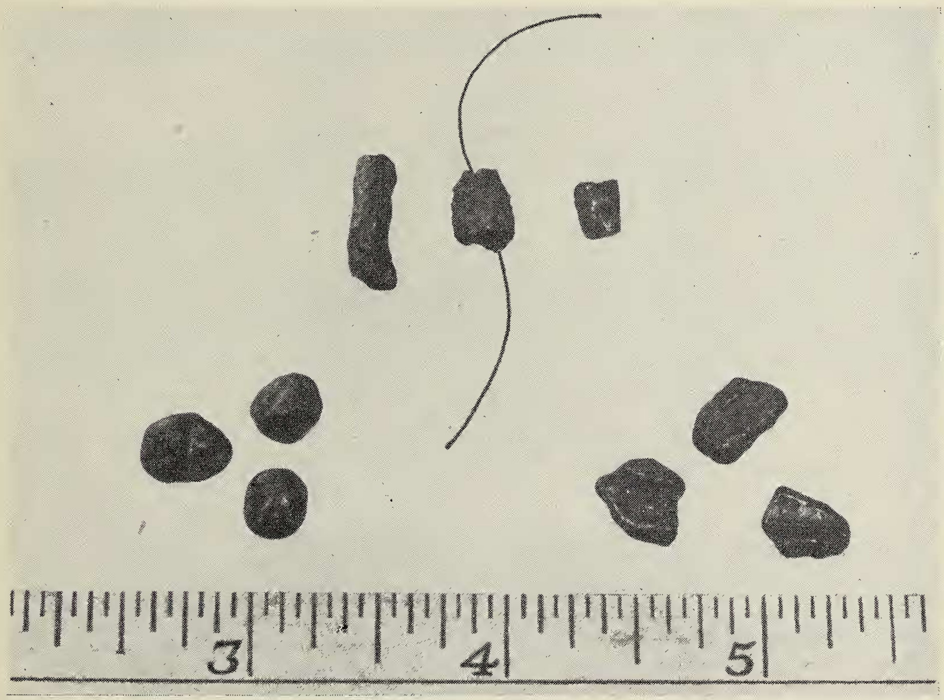

FIG. 1. Types of pyrolusite concretions found in Hawaiian soils. Lower left, spherical type; upper center, tubular, formed around roots of plants (a black thread has been passed through the cavity left by a decayed root); lower right, the irregular type formed in the larger openings in the soil.

TABLE 1

THE CHEMICAL COMPOSITION OF SOME MANGANIFEROUS SOILS AND PYROLUSITE CONCRETIONS SEPARATE FROM SAME SOILS

SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO_2
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
MANGANIFEROUS SOILS					
Soil No. 1	31.32	32.00	16.10	2.90	2.58
2	31.72	36.60	16.55	2.85	5.22
3	31.28	36.90	16.20	2.90	1.79
CONCRETIONS FROM SOILS					
Concretion 1	19.87	33.78	10.74	1.56	28.04
2	17.54	26.23	11.15	2.02	30.03
3	17.38	25.70	13.70	2.34	30.78
4	18.91	27.07	10.88	1.55	30.18
5	16.83	29.36	9.85	2.29	29.88
6	15.80	31.34	12.69	1.33	27.93
7	16.86	28.37	13.25	1.33	28.63

TABLE 2

THE CHEMICAL ANALYSES OF DIFFERENT TYPES OF PYROLUSITE CONCRETIONS FOUND IN HAWAIIAN SOILS

TYPE OF CONCRETION	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO_2
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Spherical 1	15.88	33.12	14.20	2.65	31.13
2	16.67	32.26	14.26	2.61	29.45
3	17.27	32.73	4.47	1.65	33.96
4	21.24	28.92	9.16	2.26	29.39
5	19.94	29.92	7.47	1.91	34.16
6	11.21	31.89	9.46	2.18	34.02
7	14.38	39.76	0.66	2.63	39.76
Average	16.66	32.66	8.53	2.27	33.12
Tubular 1	11.64	25.60	18.66	2.74	23.83
2	14.53	24.86	16.73	2.39	28.73
3	9.50	33.10	17.77	3.22	23.13
4	10.82	30.59	16.05	2.61	24.78
5	15.93	26.25	11.54	2.71	31.09
6	17.14	31.94	11.37	2.79	26.30
7	15.68	27.81	10.57	2.22	31.37
Average	13.61	28.59	14.67	2.79	27.03
Irregular 1	10.95	34.13	4.76	2.38	25.11
2	14.33	29.08	6.24	2.27	28.06
3	13.06	15.29	8.12	1.88	44.19
4	17.54	24.97	15.15	3.37	28.90
5	17.96	25.82	13.44	3.31	30.82
6	19.79	26.67	10.06	2.24	32.70
Average	15.60	26.00	9.63	2.57	31.63

less water of hydration or a greater purity in the minerals making up the concretions. It would appear that the composition of the pyrolusite concretions is not affected by the type of deposition since there is greater variation between individual concretions within the type than between the types.

The nature of the deposition of the MnO_2 around certain specific nuclei rules out the submergence hypothesis of origin. The formation of the concretions has been the result of soil weathering since they have been precipitated in those soils which have developed under alternating wet and dry conditions. The alternating wet and dry condition of the soil is essential in the development of concretions of pyrolusite and ferruginous-pyrolusite concretions since it provides the conditions for the solution, leaching, oxidation, and precipitation of the manganese which are necessary for the process. Kelley (1912) has pointed out that pyrolusite concretions are not found in soils which received sufficient rainfall to keep the soil in a moist condition throughout the year.

SUMMARY

Pyrolusite concretions are found in small areas within the manganiferous soils, the red soils, of the Hawaiian Islands. These concretions are found in the soils of the drier regions which have definite wet and dry seasons. The origin of the pyrolusite concretions in these soils has been the subject of some speculation. Two hypotheses have been proposed: namely, that the concretions were developed during a period of submergence of the islands, and that they have developed as a result of the weathering of lavas at higher elevations and the subsequent leaching of the manganese to lower elevations where it has been precipitated.

Pyrolusite concretions have been found which have developed around the roots of a shrub. An appreciable portion of the concretions found in Hawaiian soils has been developed by the deposition of MnO_2 around the roots of plants. Further studies suggest that the spherically shaped concretions have been formed by the deposition of MnO_2 around very small nuclei. The irregularly shaped concretions have been deposited in cracks in the soil, earthworm burrows, and larger openings in the soil.

The concretions have been analyzed; their MnO_2 content varies from 23.1 to 44.2 per cent.

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